Quarterly Progress Report

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FUNDAMENTAL STUDIES OF THE METALLURGICAL, ELECTRICAL, AND OPTICAL PROPERTIES OF GALLIUM PHOSPHIDE

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Prepared For

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
LEWIS RESEARCH CENTER
CLEVELAND, OHIO

Work Performed By

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PROJECT 5003: ELECTRICAL AND OPTICAL PROPERTIES OF III-V COMPOUNDS

National Aeronautics and Space Administration Grant NSG 555
Project Leader: G. L. Pearson
Staff: Douglas H. Loescher

The purpose of this project is the fabrication and testing of gallium phosphide diodes. Both the electrical and the luminescent properties of the diodes will be measured. Also, the effect of simultaneous application of high temperatures and large reverse biases will be studied. Both alloyed and diffused diodes will be examined.

Since the report of June 1964, more work has been done on the fabrication of diffused diodes. It has been found that the surface damage seen on a wafer after 800 ^{o}C zinc diffusions is caused by the distillation of zinc onto the wafer. It was formerly believed that the damage was caused by the evaporation of phosphorus from the surface of the wafer. Calculations, based on the partial pressure of phosphorus over gallium phosphide at 800 ^{o}C, suggested that less than one percent of the phosphorus atoms in the first mono-layer should be lost by evaporation. This calculation is supported qualitatively by an experiment in which a piece of polished gallium phosphide was heated in an evacuated ampule containing no zinc. There was no detectable surface damage. On the basis of these results we have begun doing zinc diffusions in the smallest possible ampule, thereby reducing the amount of zinc required; and also we quench the ampule in such a way that the zinc does not condense on the sample. These two procedures have led to satisfactory zinc diffusions with no apparent surface damage.

The search for good contact materials was also continued. An alloy of gold and zinc gives good contact to p-type material. An alloy of indium-1.5 percent tellurium gives good contact to n-type material. The indium-tellurium alloy seems to give better ohmic contact than the frequently employed silver-tellurium alloy.

Hall measurements and measurements of surface barrier capacitance are being used to determine carrier concentration. The carrier concentration of one Te-doped sample was, at room temperature, 2×10^{18}; the activation energy was 0.055 eV. This value of activation energy is in close agreement with the value determined by Thomas et al [Ref. 1]. The carrier concentration deduced from the capacitance of the surface barrier diode was 3.6×10^{18}. The agreement between the carrier concentrations measured in the two ways is reasonable.

The diodes fabricated from the above crystal have breakdown voltages between eight and ten volts and show red luminescence. There is a large apparent series resistance in the forward direction; for example, a diode carrying one milliamp might be dissipating five milliwatts.

In the future we plan to examine the emission spectrum of the diodes and also plan to determine the structure of the p-n junction.

PROJECT 5005: BAND STRUCTURE OF GALLIUM PHOSPHIDE

National Aeronautics and Space Administration
Grant NsG 555
Project Leader: J. L. Moll
Staff: R. C. Eden

The objective of this project is the experimental determination of the electronic band structure of gallium phosphide over a wide range of temperature.

In the past quarter, further analysis of the optical absorption data for gallium phosphide in the region of the band edge has been carried out. It has been found that if reflection and "free-carrier" corrections to the optical density data are carefully made, the lower "foot" structure theoretically predicted may be observed on curves of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for low temperatures. This additional structure permits the direct evaluation of the energy gap and phonon energy or energies involved in the transition at that temperature.

The reflectivity and "free-carrier" corrections are determined by extrapolating the below band-gap absorption data (due to these causes alone) on a best-fit curve to the band-edge region. The results obtained by this method are shown in Fig. 57 for 0 ^{o}C. The lower structure, consisting of a "double foot," can best be explained by a two-phonon model. Here two competing absorption processes are going on, one with a phonon

[1] D. G. Thomas, M. Gershenzon, F. A. Trumbore, "Pair Spectra and "Edge" Emission in Gallium Phosphide," Phys. Rev. 133, p. A269, Jan 6, 1964.

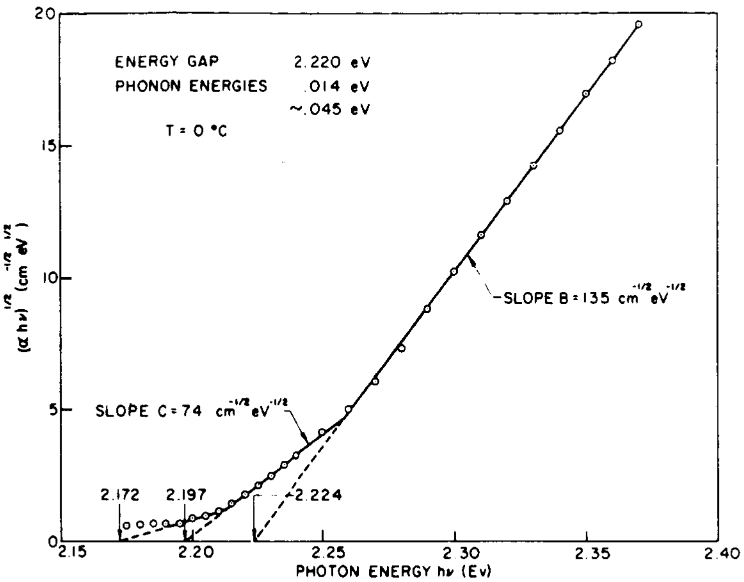

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FIG. 57. GALLIUM PHOSPHIDE ABSORPTION CURVE, $(\alpha\ h\nu)^{1/2}$ versus $h\nu$ for T = 0 °C.

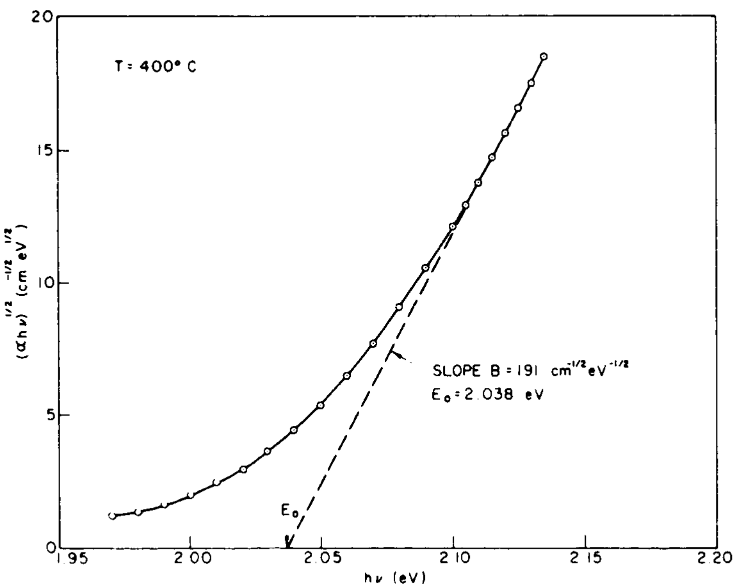

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FIG. 58. GALLIUM PHOSPHIDE ABSORPTION CURVE, $(\alpha\ h\nu)^{1/2}$ versus $h\nu$ for T = 400 °C.

energy of 0.014 eV and the other with approximately 0.045 eV. The curve for -50 ^{o}C shows similar structure but at temperatures of 100 ^{o}C and above, this lower structure is obscured by an exponential "tail" on the absorption curve as reported previously. An example of this type of curve is included for comparison in Fig. 58. Further analysis of this high-temperature data using the results obtained at 0^{o} and -50^{o} to try to obtain the energy gap more accurately is being carried out.

In addition to this absorption work, a vacuum chamber for the measurement of the ultraviolet reflectivity of samples has been constructed and is being prepared for use. In addition, a computer program for analyzing such reflectivity data to obtain the optical constants of the sample material has been prepared and checked out.

PROJECT 5006: EPITAXIAL GROWTH OF GaP

National Aeronautics and Space Administration
Grant NsG 555
Project Leaders: G. L. Pearson, J. L. Moll
Staff: T. Koike

The purpose of this project is to apply the close-spaced epitaxial growth technique to GaP in order to study its optical and electrical properties.

GaP is transported to a GaAs substrate in the system described in the previous report. All depositions were made on the [100] surface of GaAs. During this quarter we acquired the following optimum growing conditions:

(1)	Source temperature	970 ~ 980 ^{o}C
(2)	Substrate temperature	930 ~ 940 ^{o}C
(3)	Temperature difference	30 ~ 40 ^{o}C
(4)	Spacing	40 ~ 50 mils
(5)	Flow rate of hydrogen	4 ~ 5 cc/min.

We found that the initial temperature of the interface of the two carbon blocks determined the structure of the deposited crystals. The temperature distribution in the carbon blocks are not uniform but higher at the interface at the beginning of the experiment until it reaches thermal equilibrium. Therefore, extreme care must be taken to maintain the optimum operating conditions and the use of a temperature controller is advisable. If the temperature is too high, the grown crystal is usually accompanied by a large number of dislocations and grain-boundaries. On the contrary, if the temperature is too low, the grown crystal becomes amorphous. The transport of GaP in the presence of water is believed to be [Ref. 1]

$$2GaP + H_2O \rightleftarrows Ga_2O + H_2 + P_2 \quad . \tag{1}$$

We have found that the weight loss from the source during the deposition is a maximum at the optimum operating conditions. In Fig. 59, the weight loss from the source per hour is plotted against the substrate temperature. The temperature was measured by a thermocouple embedded in one of the carbon blocks and by an optical pyrometer. The temperature difference between the source and the substrate was kept 30 ~ 40 °C and the flow rate of the hydrogen gas was 5 ± 1 cc/min. The efficiency of the deposition also showed a similar result. This result seems very reasonable from the viewpoint of the chemical reaction which takes place in the reaction tube. The flow rate of the hydrogen gas was found rather insensitive to the amount of transport from the source onto the substrate since the hydrogen gas was passed over water and through the ice-salt bath (-21.3 °C) in order to obtain the saturated water vapor pressure into the system. However, a higher rate of hydrogen flow tends to disturb this saturating condition and the grown crystal becomes oxidized. This oxidized layer is attributed to excessive water content in the reaction tube introduced by the higher rate of the hydrogen gas.

The temperature difference is also very closely related to the growing condition and should be considered in relation to the source and the substrate temperatures. At the source the temperature should be high enough so as to induce the reaction

$$2GaP + H_2O \rightarrow Ga_2O + H_2 + P_2 \;, \tag{2}$$

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[1] Thurmond, C. D., and C J. Frosch, Electromechanical Society, Fall Meeting, New York, New York (1963).

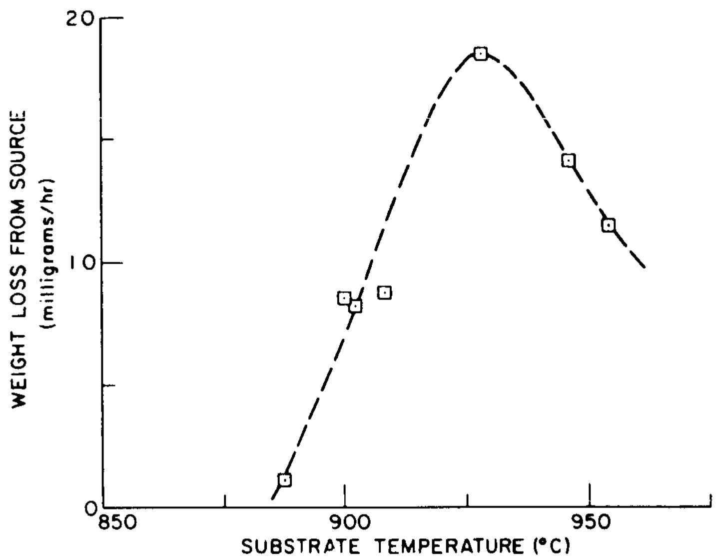

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FIG. 59. WEIGHT LOSS FROM THE GaP SOURCE VS THE SUBSTRATE TEMPERATURE DURING THE DEPOSITION. $\Delta T = 30 \sim 40\ ^{o}C$. Flow rate = $5 \neq 1$ cc/min. Spacing $\doteq$ 40 ~ 50 mils.

and at the substrate the temperature should be lower so that the decomposition of Ga_2O can take place:

$$Ga_2O + H_2 + P_2 \rightarrow 2GaP + H_2O \ . \tag{3}$$

Then, we have an impression that as long as the temperature of the substrate is appropriate the rate of decomposition of Ga_2O from the vapor phase and the rate of deposition onto the surface of the substrate occur according to Eq. (3), we can increase the temperature difference to a higher value. However, the temperature difference is limited by other factors. If the temperature difference is increased, the resulting temperature distribution in the carbon blocks becomes steep and the response of the system to a sudden change of the input rf power becomes undesirable.

The spacing of the system is also considered in relation to the other parameters. Since the temperature difference is obtained by the relative positions of the carbon blocks and the rf coil, a closer spacing tends to give no temperature difference at thermal equilibrium. Therefore, the spacing should be so chosen that the resultant temperature difference at thermal equilibrium is the optimum value.

The system has been operating successfully under these optimum conditions and a growth rate of over 2 mils per hour was achieved.

We were not able to grow a mixture of GaP and GaAs during this quarter because suitable source material was not available. However, future work will be concentrated on this problem.

PROJECT 5108: A STUDY OF $GaAs_x P_{1-x}$

National Aeronautics and Space Administration Grant NSG 555
Project Leader: Gerald L. Pearson
Staff: Yen-sun Chen

The object of this project is to evaluate the optical, electrical and metallurgical properties of the $GaAs_xP_{1-x}$ alloy. Among evaluations of particular interest to us are the investigation of the crystal structure and its imperfections by the Kossel line technique and by that of the lattice absorption spectra as the mole fraction of GaAs and x, varies from 0 to 1.

Efforts in this quarter have been concentrated on 1) growing undoped $GaAs_xP_{1-x}$ crystals and 2) setting up the optical system and measuring the reststrahlen bands of the alloy in the region of 25μ--40μ.

A. CRYSTAL GROWTH

The method of open tube epitaxial vapor growth is employed. This method was originally developed in this laboratory by Gibbons and Prehn [Ref. 1]. A description of the system is shown in Fig. 65.

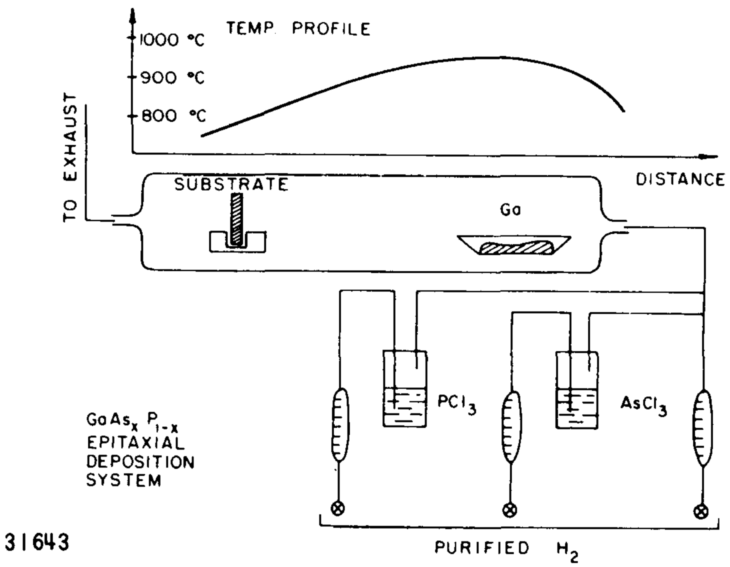

FIG. 65. $GaAs_xP_{1-x}$ EPITAXIAL DEPOSITION SYSTEM.

A total of thirteen runs were made. These are phosphorous-rich polycrystals grown on quartz or sapphire substrates. Typical growth condition is as follows:

Substrate temp.: 765 °C with a gradient of 20 °C/cm

H_2 flow: 50 cc/min through PCl_3 at 0 °C

[1]Gibbons, J., and P. Prehn, "Epitaxial Vapor Growth of III-V Compounds," Technical Report No. 4711-1, SEL, Oct 1963.

50 cc/min through $AsCl_3$ at 25 °C

150 cc/min in total

Growth rate: 1--2μ/min

Composition: 75% P

These crystals were directly mounted on the X-ray goniometer to detect the lattice constant and hence the composition of the mixture. From the transmission data of these samples in the region of 10μ--25μ, it was observed that the effect of free carrier absorption is neglegible; thus, we believe, the concentration of the carrier is in the order of $10^{16}/cm^3$. We are, however, not satisfied with the band edge absorption of these samples; they are not comparable to that of GaP or GaAs. We expect to solve this problem and to study the two-phonon absorption bands of the alloyed crystal in detail in the coming quarter.

B. RESTSTRAHLEN BANDS

We have set up an infrared spectrometer working in the range of 1μ--40μ. Among the major parts of the system are the globar light source, the Leiss single Monochramator with a CsBr prism and the thermocouple detector with a diamond window. The absorption bands of water vapor [Ref. 2] and a thin polystyrene film were used to calibrate the system.

The system was used to detect the reststrahlen bands of $GaAs_xP_{1-x}$ by measuring the spectra of reflectivity. The references used in the region of interest are that of our Al mirror (100%) and InAs (30%). In Fig. 66, the spectra of reflectivity of five samples (x = 0, .18, .58, .71, and 1.0) are shown. In Fig. 67, we have plotted the reststrahlen bands as a function of x; the width of the band is taken at 20% of the peak value and the peak itself is marked by a dot. In contrast to data previously obtained on two-phonon absorption bands of these crystals [Ref. 3] where the bands of GaP and GaAs are believed to be superposed, we see here a continuous shift of the band from GaP to GaAs.

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[2] I. Mills, J. Scherer, B. Crawford, and M. Youngquist, "Calibration and Use of a Cesium-Iodide Prism in the Infrared," J. of the Optical Soc. of America, 45, 785 (Oct 1955).

[3] See SEL Quarterly Research Review No. 9 on this project.

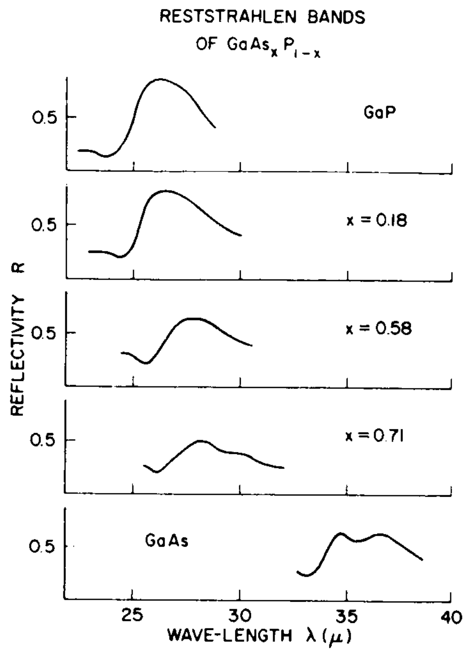

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FIG. 66. RESTSTRAHLEN BANDS OF $GaAs_xP_{1-x}$.

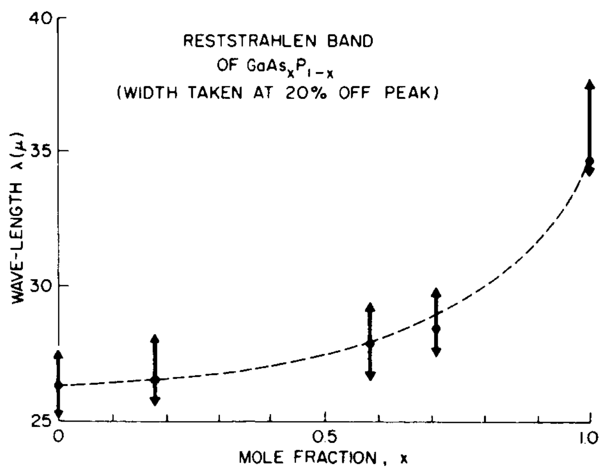

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FIG. 67. RESTSTRAHLEN BAND OF $GaAs_xP_{1-x}$ (WIDTH TAKEN AT 20 PERCENT OFF PEAK).

From this result, we shall try to analyze the values of the effective ionic charge, e*, using the theory of Szigeti, [Ref. 4]

$$\frac{e^*}{e} = \left[\frac{\omega_0^2 M A_0^3 (\epsilon_0 - \epsilon_\infty)}{16\pi}\right]^{1/2} \left(\frac{3}{\epsilon_\infty + 2}\right)$$

where M is the reduced mass of a primitive cell,

A_0 is the lattice constant,

ϵ_0 is the static dielectric constant,

and ϵ_∞ is the high-frequency dielectric constant.

It is interesting to point out that in Braunstein, Moore, and Herman's work [Ref. 5] on Si-Ge alloy, one group of their proposed short-range ordered crystal (cases 0, 1, 2', 3', 4', 5', 6', 7, 8 and 4") gives the result that the energy of the (000) optical phonon varies with the composition of alloy in the same fashion as does our experimental data in the reststrahlen bands of $GaAs_xP_{1-x}$. This group has the closest resemblance of a cluster model, since the similar atoms are grouped together in the lattice. We shall investigate this aspect further in the coming quarter.

PROJECT 5109: EPITAXIAL GROWTH OF III-V SEMICONDUCTOR COMPOUNDS

National Aeronautics and Space Administration
Grant NsG 555
Project Leader: G. L. Pearson
Staff: D. Chauvy and J. W. Allen

The purpose of this project is to examine and control the crystallographic and electrical properties of III-V compound semiconducting materials grown epitaxially by vapor deposition. Our interests have been concentrated on the compounds GaP and GaAs and on the determination of the chemical reactions involved in the deposition of these compounds from the vapor phase.

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[4] Szigeti, B., Trans. Faraday Soc., 45, 155 (1949).

[5] B. Braunstein, A. Moore and F. Herman, "Intrinsic Optical Absorption in Ge-Si Alloys," Phys. Rev., 109, 695 (1958).

The work by Mr. Chauvy is complete and a final report is in preparation. Mr. Chauvy has returned to Switzerland and J. W. Allen has recently arrived from England to serve as a research associate during the coming year. He hopes to study deep lying levels in GaP by optical and electrical methods as well as the development of materials for device purposes.